

A coordinate-free description of nonequilibrium thermodynamics

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THE EMPHASIS in nonequilibrium thermodynamics is upon such conceptual problems as (i) understanding the meaning of temperature and pressure beyond local equilibrium or (ii) obtaining the theory of thermodynamic potentials for systems not infinitesimally near to equilibrium. In order to study these problems, the present paper offers the development of an approach based upon the following entropy maximum principle: among all states having the same values of conserved variables, the equilibrium state gives the specific entropy its greatest value. The entropy maximum principle, if combined with the ideas standing behind a coordinate-free description of the thermodynamic space of nonequilibrium states, allows one to draw upon results from the critical point theory. Precisely speaking, using this theory, it is possible to find a coordinate system for the thermodynamic space such that the (specific) entropy can be written as a sum of two physically different terms: the first term represents the thermostatic entropy (which is a function of conserved variables), while the second term is given by a quadratic form depending only on "nonequilibrium variables". Due to the existence of this particularly simple representation of the specific entropy, one easily arrives at the natural definitions of temperature, pressure, and thermodynamic potentials for systems not infinitesimally near to equilibrium.

1. Introduction

IN GIBBSIAN thermostatics [1, 2], the state of a macroscopic system is described by a set of additive conserved variables (Y_1, \dots, Y_r) , denoted collectively by Y . The guiding idea is that these variables, which are sometimes called the extensive variables, are directly measurable. Given a system with a fixed amount of matter, we may single out the number of moles or molecules N as a scale factor and then introduce the intrinsic quantities $y_\beta := Y_\beta(N)^{-1}$ where $\beta = 1, \dots, r$. In the most common special case of a homogeneous chemically inert fluid, $y := (y_1, \dots, y_r)$ consists of the specific internal energy ε and the specific volume v ; hence $r = 2$.

As we know, in Gibbsian thermostatics the concept of entropy is taken for granted. Thus, to each state e of the system labeled by y there is assigned a real number $h_E(y)$ called the specific entropy. The intensive variables Π_β conjugate to y_β are introduced as derivatives of h_E . For a homogeneous chemically inert fluid, the intensity $\Pi_1 = \partial h_E / \partial \varepsilon$ is equal to the inverse of the absolute temperature T and $T\Pi_2 = T(\partial h_E / \partial v)$ can be identified with the thermodynamic pressure p .

The application of geometrical methods to thermostatics rests on the assumption that the set E of all equilibrium states of the system is a finite-dimensional differentiable manifold [3, 4].

Now, it is widely believed that even for systems in a nonequilibrium state the intrinsic conserved variables y are well-defined observable quantities. However, in order to make the information associated with the nonequilibrium state complete, one has to use, in many cases, additional thermodynamic variables to specify the properties of the system. Thus, what various approaches in the literature have typically proposed [5-12] has been to introduce a new set of real variables (z_1, \dots, z_s) , denoted collectively by z , and then to characterize the nonequilibrium state n by (y, z) . Consequently, most of the

existing formulations of thermodynamics for systems not infinitesimally near to equilibrium hinge on the postulate that the number of additional variables is finite. From the physical point of view, the universal validity of this postulate is by no means obvious, but here we do not enter into a detailed discussion of these difficult problems. Rather, we shall study the important consequences of the assumption that the set \mathbf{N} consisting of all nonequilibrium states of the system is a finite-dimensional differentiable manifold ($\dim \mathbf{N} = r + s$).

Of course, the physical interpretation of the theory calls for a clear interpretation of the variables z . For example, in extended thermodynamics of rarefied gases [5], it is tempting to set $s = 8$ and then assume that the variables z are expressed in terms of the components of the pressure deviator \mathbf{P} and the heat flux \mathbf{R} . Also, given the postulational basis of rational thermodynamics [7–9], one can consider the materials of the differential type for which the numbers z are the space-time derivatives of the local conserved variables y . Finally, we may regard the parameters z as being the internal state variables [6, 10–12]. The concept of internal state variables ⁽¹⁾ has been widely used in thermodynamics of irreversible processes [10] and in the general theory of viscoelastic and viscoplastic materials [6, 11].

The notion of entropy for gases and fluids not infinitesimally near to equilibrium is sufficiently well substantiated, at least insofar as the kinetic theory of BOLTZMANN [13, 9] and the revised kinetic theory of ENSKOG [14, 15] are concerned. In addition, the scheme based upon the existence of entropy has met with wide acceptance in the literature regarding nonequilibrium thermodynamics [16]. In our macroscopic theory, entropy is a primitive concept. We postulate that there is a sufficiently smooth function $h : \mathbf{N} \Rightarrow \mathbf{R}$ which ⁽²⁾ assigns the specific entropy $h(n)$, i.e., the entropy per mole (particle), to each nonequilibrium state $n \in \mathbf{N}$ labeled by (y, z) .

In order to formulate and study our main problem, it is now necessary to review some aspects of the notation employed throughout the paper. Let $n \in \mathbf{N}$ be the state labeled by (y, z) . Then we postulate ⁽³⁾ that n is an equilibrium state if and only if $z_\beta = 0$ for each β ($\beta = 1, \dots, s$). Among other things, this means that we agree to regard henceforth the set \mathbf{E} consisting of all equilibrium states of the system as a certain assigned submanifold of \mathbf{N} . With these preliminaries, we are ready to define the projection π of \mathbf{N} onto \mathbf{E} . Namely, the value of π at n is uniquely determined by the condition that if the variables (y, z) specify n , then the variables $(y, 0)$ specify $\pi(n)$, the image of n under π . For $e \in \mathbf{E}$, we shall refer to $\pi^{-1}(\{e\}) := \{n \in \mathbf{N} \mid \pi(n) = e\} \subset \mathbf{N}$ as the inverse image of $\{e\}$ by π . The state $n \in \mathbf{N}$ is said to be consistent with a state $e \in \mathbf{E}$ if $n \in \pi^{-1}(\{e\})$. Alternatively, we say that the state $\pi(n)$ has the same values of conserved variables y as n . Then we may call $\pi(n)$ the equilibrium state corresponding to n . There is nothing unnatural about this terminology. In Grad's formulation of the kinetic theory of gases [13, 9], the similar terminology, although not discussed or mentioned only vaguely, is inherently present in the characterization of the infinite-dimensional space of nonequilibrium states.

⁽¹⁾ Some authors [12] use the term "hidden variables" or "hidden coordinates".

⁽²⁾ The symbol \mathbf{R} denotes the set of real numbers.

⁽³⁾ This postulate is sufficiently general to represent most of the physically important systems, although (in all probability) it cannot be valid for viscoplastic materials [6, 10, 11]. Such materials, however, will not be discussed here.

The states having the same values of conserved variables serve as comparison states for the entropy maximum principle⁽⁴⁾. Precisely speaking, we express this fundamental principle by postulating that among all states consistent with $e \in E$, the equilibrium state e gives $h : \mathcal{N} \Rightarrow \mathbb{R}$ its greatest value. The main objective of this paper is the systematic development of a coordinate-free description of the thermodynamic space \mathcal{N} of nonequilibrium states as well as of the entropy maximum principle. The extremal property of the specific entropy, which is an indispensable element of our generalization of Gibbsian thermostatics [1, 2], allows us to draw upon results from the Morse critical point theory [3, 4, 21]. We will show that this theory (cf., e.g., the lemma of Morse; p. 493 in Ref. [4]), if combined with the ideas standing behind the geometrical interpretation [3, 4] of the finite-dimensional space \mathcal{N} , is very useful in obtaining a large number of thermodynamic potentials and identities for systems not infinitesimally near to equilibrium. Moreover, we shall focus upon such conceptual problems as (i) understanding the meaning of temperature and pressure beyond local equilibrium or (ii) determining the conditions under which the differential of h (the extended Gibbs relation) can be represented by a particularly simple formula.

Loosely speaking, what we show is that the methods established by the critical point theory [3, 4] serve to generate a privileged class of coordinates (y, z) for \mathcal{N} . In view of the existence of such a class of coordinates, the specific entropy h can be written as a sum of two physically different terms: the first term, denoted by $h_E(y)$, represents the thermostatic entropy (which is a function of the conserved variables y), while the second term is given by a quadratic form $-\sum_{\beta=1}^s (z_\beta)^2$ depending only on the nonequilibrium variables z . Using this representation of the specific entropy h , it is easy to prove that the derivatives of h with respect to y are functions independent of z . Thus, in this way of thinking, Gibbsian thermostatics [1, 2] is not to be viewed simply as a first approximation to the full description of the system, but, instead, as an exact theory valid for a suitably chosen parametrization of the space of nonequilibrium states. Furthermore, all of the classic assertions about the (free) energy minimum principles [2, 7] will find their places as clearly stated and mathematically proved theorems in the above-mentioned parametrization. The same remark concerns the well-known formalism of Legendre transformations [2], which does not fail to exist when applied to the coordinate system congruent with the geometrical properties of \mathcal{N} . (The manifold \mathcal{N} has the structure of the differentiable fibre bundle [4]; in this context, see Appendix B.) Finally, it seems to us that our preliminary results can be related to many existing presentations of thermodynamics, and all of them yield the same conceptual framework upon which a systematic characterization of various macroscopic theories may be based.

The layout of this paper is as follows. Section 2 contains a short description of the structure of the space of nonequilibrium states. Section 3 and Appendix A are devoted to a discussion of the relationship between the entropy maximum principle and the critical point theory [3, 4]. In Section 4, we analyse the extended Gibbs relation and the (free) energy minimum principles. Since this analysis can be carried out in a step-by-step analogy to that in Gibbsian thermostatics, we confine ourselves to giving the final answer with a few explanatory remarks. A very simple example illustrating our general considerations is

⁽⁴⁾ If a macroscopic approach is compatible with the kinetic theory of gases, then, in many cases, the entropy maximum principle is a rigorous consequence of the definition of the specific entropy in terms of the distribution function (cf., e.g., Refs. [9, 13, 17, 18]).

found in Sec. 5. We conclude the paper with final remarks of Sec. 6. In Appendix B, we discuss the structure of \mathbf{N} from the standpoint of the theory of differentiable fibre bundles [4].

2. Structure of the space of nonequilibrium states

We now proceed to list the basic postulates and definitions, the basis of nonequilibrium thermodynamics, amplified by short comments that are required for the clarification of the formal statements.

a. The set \mathbf{N} consisting of all nonequilibrium states of a macroscopic system is a finite-dimensional, differentiable manifold; $\dim \mathbf{N} = r + s$. (The n will symbolize the elements of \mathbf{N} .) The basic content of this postulate should be more or less obvious. The space \mathbf{N} is locally Cartesian, and the passage from one coordinate system to another is smooth in the overlapping region. The dimension of \mathbf{N} gives the number of independent degrees of freedom.

b. In order to distinguish an equilibrium configuration within the class of all possible ones, we postulate that there is a submanifold of \mathbf{N} , denoted by \mathbf{E} , such that if e belongs to \mathbf{E} , then e represents the equilibrium state of the system; $\dim \mathbf{E} = r$.

c. For a certain finite-dimensional manifold \mathbf{G} ($\dim \mathbf{G} = s$), the product manifold $\mathbf{E} \times \mathbf{G}$ is diffeomorphic to \mathbf{N} . We use the symbols g and (e, g) to signify the elements of \mathbf{G} and $\mathbf{E} \times \mathbf{G}$, respectively. A diffeomorphism from $\mathbf{E} \times \mathbf{G}$ onto \mathbf{N} is represented by the map $D : \mathbf{E} \times \mathbf{G} \rightarrow \mathbf{N}$. The symbol $D(e, g)$ will stand for the image of (e, g) under D . We shall refer to $D(e, \mathbf{G}) \subset \mathbf{N}$ as the image of the set $\{e\} \times \mathbf{G} \subset \mathbf{E} \times \mathbf{G}$ by D . The introduction of \mathbf{G} and D allows us to characterize and classify the nonequilibrium states. For example, using the "projection" π of \mathbf{N} onto \mathbf{E} defined by $\pi(n) = \pi(D(e, g)) := e$, we may obtain an exhaustive partition of \mathbf{N} into disjoint subsets, the equivalence classes, such that the equivalence class to which an arbitrary state $n \in \mathbf{N}$ belongs is equal to $\pi^{-1}(\{e\}) := \{n' \in \mathbf{N} \mid \pi(n') = e\}$ where $e = \pi(n)$. Clearly, $\pi^{-1}(\{e\}) = D(e, \mathbf{G})$. From the physical point of view, the equivalence class $\pi^{-1}(\{e\})$ is made up of all nonequilibrium states n consistent with a given equilibrium state e . Alternatively, we may call $\pi(n)$ the equilibrium state corresponding to n .

d. Since the equilibrium state $\pi(e)$ corresponding to $e \in \mathbf{E}$ should be equal to e , we assume that there exists exactly one element g_0 of \mathbf{G} such that if e is an arbitrary member of \mathbf{E} , then $D(e, g_0) = e$. (Thus, indeed, π is a projection of \mathbf{N} onto $\mathbf{E} \subset \mathbf{N}$, because $\pi^2 = \pi$.) We are aware of the fact that this assumption is not a valid statement when applied to viscoplastic materials [6, 10, 11], but it represents a sufficiently good proposition for many other systems of physical interest.

We shall close our discussion of the structure of \mathbf{N} by providing a very simple

EXAMPLE. Let us consider a three-dimensional, classical, moderately rarefied, simple, monatomic gas consisting of molecules of unit mass. The following variables, direct idealizations from daily experience, are the primitive elements of nonequilibrium thermodynamics of the above-mentioned system [5]:

| Name | Symbol |
|--|---------------|
| specific energy (internal energy per particle) | ε |
| specific volume (per particle) | v |
| pressure deviator | \mathbf{P} |
| heat flux | \mathbf{R} |

After introducing the primitive quantities, the members of \mathbf{N} , \mathbf{E} , and \mathbf{G} can be constructed in their terms:

$$(2.1) \quad \begin{aligned} n &:= (\varepsilon, v, \mathbf{P}, \mathbf{R}) \in \mathbf{N}, & e &:= (\varepsilon, v, \mathbf{0}, \mathbf{0}) \in \mathbf{E} \subset \mathbf{N}, \\ g &:= (\mathbf{P}, \mathbf{R}) \in \mathbf{G}, & g_0 &:= (\mathbf{0}, \mathbf{0}) \in \mathbf{G}. \end{aligned}$$

The action of $D : \mathbf{E} \times \mathbf{G} \Rightarrow \mathbf{N}$ upon $(e, g) \in \mathbf{E} \times \mathbf{G}$ is given by

$$(2.2) \quad D(e, g) = D((\varepsilon, v, \mathbf{0}, \mathbf{0}), (\mathbf{P}, \mathbf{R})) := (\varepsilon, v, \mathbf{P}, \mathbf{R}) = n.$$

Using Eqs. (2.1), we conclude that

$$(2.3) \quad \begin{aligned} \dim \mathbf{E} = r = 2, & \quad \dim \mathbf{G} = s = 8, \\ \dim \mathbf{N} = r + s = 10. \end{aligned}$$

Returning to the definition of the projection $\pi : \mathbf{N} \Rightarrow \mathbf{E}$, we arrive at $\pi(n) = \pi((\varepsilon, v, \mathbf{P}, \mathbf{R})) = (\varepsilon, v, \mathbf{0}, \mathbf{0}) = e$.

3. The entropy maximum principle and the Morse critical point theory

In this paper, the specific entropy (per particle) is a primitive concept, characterized by the following two axioms:

e. There exists a scalar field $h : \mathbf{N} \Rightarrow \mathbf{R}$ which assigns to each $n \in \mathbf{N}$ a real number $h(n)$ called the specific entropy. In order that all the mathematical operations of this paper be well defined, by $h : \mathbf{N} \Rightarrow \mathbf{R}$ we shall always mean a sufficiently smooth scalar field. For example, the term “sufficiently smooth” means C^∞ , but is used in preference to C^∞ , because in fact we do not require “infinite” smoothness.

f. The equilibrium state $D(e, g_0) = e$ gives h the greatest value it can attain for all states $n \in D(e, \mathbf{G}) = \pi^{-1}(\{e\})$ consistent with e (the *entropy maximum principle*). Precisely speaking, if e is an arbitrary member of \mathbf{E} , then $h(D(e, g)) \leq h(D(e, g_0))$ for every $g \in \mathbf{G}$; equality holds if and only if $g = g_0$.

Now, combining Axioms (a)–(f) with the results established by the *critical point theory* [3, 4, 21] (in this context, see the lemma of Morse as formulated, e.g., on p. 493 in Ref. [4]), we arrive at the main conclusion of this paper:

THEOREM. *Let \mathbf{E} be a globally Cartesian manifold. Under Axioms (a)–(f), there is a subset ⁽⁵⁾ \mathcal{N} of \mathbf{N} and a coordinate system $(y_1, \dots, y_r, z_1, \dots, z_s)$ on \mathcal{N} such that*

- (A) *the manifold \mathbf{E} is a proper subset of \mathcal{N} ;*
- (B) *if $(y_1, \dots, y_r, z_1, \dots, z_s)$ are coordinates of $e \in \mathbf{E}$, then $z_\beta = 0$ for each β ($\beta = 1, \dots, s$);*
- (C) *if $(y_1, \dots, y_r, z_1, \dots, z_s)$ are coordinates of $n \in \mathcal{N} \setminus \mathbf{E}$, then $z_\beta \neq 0$ for some β ($\beta = 1, \dots, s$);*
- (D) *the restriction of $h : \mathbf{N} \Rightarrow \mathbf{R}$ to \mathcal{N} is a rule which assigns to each state $n \in \mathcal{N}$ determined (labeled) by ⁽⁶⁾ $(y_1, \dots, y_r, z_1, \dots, z_s)$ a real number*

$$(3.1) \quad h_{\mathcal{N}}(y_1, \dots, y_r, z_1, \dots, z_s) := h_{\mathbf{E}}(y_1, \dots, y_r) - \sum_{\beta=1}^s (z_\beta)^2$$

⁽⁵⁾ This subset is an open submanifold of \mathbf{N} ($\dim \mathcal{N} = r + s$).

⁽⁶⁾ The collection of real variables $(y_1, \dots, y_r, z_1, \dots, z_s)$ is said to determine (label) $n \in \mathcal{N}$ if $(y_1, \dots, y_r, z_1, \dots, z_s)$ are coordinates of n .

identified with the specific entropy $h(n)$;

(E) in the definition (3.1), the $h_E(y_1, \dots, y_r)$ represents the specific entropy $h(e)$ assigned to the equilibrium state e labeled by $(y_1, \dots, y_r, 0, \dots, 0)$.

Proof. A sketch of the proof of this theorem is given in Appendix A.

The theorem just formulated shows that the specific entropy as given by (3.1) is compounded of two parts, one of which arises from the thermostatic effects, and the second from the nonequilibrium ones. Indeed, the first term on the r.h.s. of (3.1), which depends only on the conserved variables (y_1, \dots, y_r) , is rather obviously the specific entropy according to thermostatics; the second nonequilibrium term is more explicit, because it represents the quadratic form completely independent of y .

Looking back at the example [5] described in Sec. 2, let us assume that the specific entropy h is a sufficiently smooth function ⁽⁷⁾ of $(\varepsilon, v, \mathbf{P}, \mathbf{R})$:

$$(3.2) \quad h = h(\varepsilon, v, \mathbf{P}, \mathbf{R}).$$

One (generally accepted) property of Eq. (3.2) suffices as a basis for easy proofs of the rests: among all states $(\varepsilon, v, \mathbf{P}, \mathbf{R})$ having the same values of ε and v , the equilibrium state $(\varepsilon, v, \mathbf{0}, \mathbf{0})$ yields the greatest specific entropy h . Indeed, from our theorem it follows that there is an open submanifold \mathcal{N} of \mathbf{N} and a coordinate map $\hat{\mathfrak{z}} = (\hat{\mathfrak{z}}_1, \dots, \hat{\mathfrak{z}}_{10})$ on \mathcal{N} such that if $(y_1, y_2, z_1, \dots, z_8)$ are coordinates of $(\varepsilon, v, \mathbf{P}, \mathbf{R}) \in \mathcal{N}$, then we can substitute the inverse of

$$(3.3) \quad \begin{aligned} y_1 &= \hat{\mathfrak{z}}_1(\varepsilon, v, \mathbf{P}, \mathbf{R}) := \varepsilon, \\ y_2 &= \hat{\mathfrak{z}}_2(\varepsilon, v, \mathbf{P}, \mathbf{R}) := v, \\ z_\beta &= \hat{\mathfrak{z}}_{\beta+2}(\varepsilon, v, \mathbf{P}, \mathbf{R}), \quad \beta = 1, \dots, 8 \end{aligned}$$

into (3.2), so obtaining

$$(3.4) \quad h = h_E(\varepsilon, v) - \sum_{\beta=1}^8 (z_\beta)^2,$$

where (we consider here a simple gas consisting of molecules of unit mass; the k_B is Boltzmann's constant)

$$(3.4') \quad h_E(\varepsilon, v) = \text{const} + k_B \ln(v\varepsilon^{3/2}).$$

The domain $\mathcal{N} \subset \mathbf{N}$ over which the real-valued functions $\hat{\mathfrak{z}}_\beta : \mathcal{N} \Rightarrow \mathbf{R}$, $\beta = 1, \dots, 10$, are defined and have certain properties of smoothness depends on the choice of the *fundamental equation* (3.2). In any event, $(\mathbf{P}, \mathbf{R}) = (\mathbf{0}, \mathbf{0})$ if and only if $z_\beta = 0$ for any β ($\beta = 1, \dots, 8$).

4. The extended Gibbs relation and the energy minimum principles

Obviously, the specific entropy $h_N(y, z)$ as given by Eq. (3.1) is differentiable with respect to $y := (y_1, \dots, y_r)$ and $z := (z_1, \dots, z_s)$, and we obtain for the differential of h_N the following, particularly simple formula:

$$(4.1) \quad dh_N = \sum_{\beta=1}^r \Pi_\beta dy_\beta - 2 \sum_{\beta=1}^s z_\beta dz_\beta.$$

⁽⁷⁾ For the sake of simplicity, here we use the same symbol to denote a function and its value.

Here the intensity Π_β conjugate to y_β is defined by

$$(4.1') \quad \Pi_\beta := \frac{\partial h_N}{\partial y_\beta} = \frac{\partial h_E}{\partial y_\beta} \quad (\beta = 1, \dots, r).$$

We call (4.1) the *extended Gibbs relation*. Equation (4.1') evidently has the form of the well-known expression of Gibbsian thermostatics, because $h_E(y)$ is the *equilibrium specific entropy and the intensities Π_β depend actually only on the local conserved variables y* . Even more, this is one of many instances in which thermostatics is readily adapted to nonequilibrium thermodynamics and, in fact, an indication that the extended Gibbs relation truly deserves this name.

In the important case of a chemically inert fluid, Eq. (4.1) reduces to

$$(4.2) \quad dh_N = \frac{1}{T} d\varepsilon + \frac{1}{T} p dv - 2 \sum_{\beta=1}^s z_\beta dz_\beta,$$

where

$$(4.2') \quad \frac{1}{T} := \frac{\partial h_N}{\partial \varepsilon} = \frac{\partial h_E}{\partial \varepsilon},$$

$$(4.2'') \quad \frac{1}{T} p := \frac{\partial h_N}{\partial v} = \frac{\partial h_E}{\partial v}.$$

Thus we are able to state the theorem that for a suitably chosen class of coordinate maps on \mathcal{N} , $\partial h_N / \partial \varepsilon$ and $\partial h_N / \partial v$ are the same functions of ε and v as in equilibrium. Due to this fact, $\partial h_N / \partial \varepsilon = \partial h_E / \partial \varepsilon > 0$ and we shall refer to T as the temperature and to p as the pressure. Clearly, using the well-known axioms of thermostatics, we conclude that (4.2') is invertible for ε as a function of T and v . The resulting equation $\varepsilon = \varepsilon(T, v)$ can be called a *caloric equation of state* (valid for systems not infinitesimally near to equilibrium). All this we deduced without use of any information beyond that which directly arises from the (generally accepted) properties of smoothness and the entropy maximum principle.

If we introduce the specific free energy ψ_N ,

$$(4.3) \quad \psi_N(T, v, z) := \varepsilon(T, v) - T h_N(\varepsilon(T, v), v, z),$$

then by (4.2)

$$(4.4) \quad h_N = -\frac{\partial \psi_N}{\partial T}, \quad p = -\frac{\partial \psi_N}{\partial v}, \quad z_\beta = \frac{1}{2T} \frac{\partial \psi_N}{\partial z_\beta},$$

so that the differential of ψ_N becomes

$$(4.5) \quad d\psi_N = -h_N dT - p dv + 2T \sum_{\beta=1}^s z_\beta dz_\beta.$$

In addition, we may conclude from (4.3) and

$$(4.6) \quad h_N(\varepsilon, v, z) = h_E(\varepsilon, v) - \sum_{\beta=1}^s (z_\beta)^2$$

that of all states (T, v, z) with given values of T and v , that corresponding to zero values of z_β has the least specific free energy ψ_N (the free energy minimum principle).

Let $\varepsilon = \hat{\varepsilon}(h_E, v)$ be a solution for ε of the equation $h_E = h_E(\varepsilon, v)$ (this equation is well known in thermostatics). Returning to (4.6), we may express h_E in terms of (h_N, z)

and obtain

$$(4.7) \quad \varepsilon = \varepsilon(h_N, v, z) := \widehat{\varepsilon} \left[h_N + \sum_{\beta=1}^s (z_\beta)^2, v \right].$$

Hence

$$(4.8) \quad T = \frac{\partial \varepsilon}{\partial h_N}, \quad p = -\frac{\partial \varepsilon}{\partial v}, \quad z_\beta = \frac{1}{2T} \frac{\partial \varepsilon}{\partial z_\beta},$$

$$d\varepsilon = T dh_N - p dv + 2T \sum_{\beta=1}^s z_\beta dz_\beta.$$

Now, it is not difficult to see that $\partial \varepsilon / \partial h_N > 0$. Indeed, the function $\partial \varepsilon / \partial h_N$ is equal to $\partial \widehat{\varepsilon} / \partial h_E = (\partial h_E / \partial \varepsilon)^{-1}$ and, according to the generally accepted assumptions of thermostatics, the derivative of $h_E(\varepsilon, v)$ with respect to ε must be positive. Then, beginning from (4.7) and $\partial \varepsilon / \partial h_N > 0$, we find that *among all states (h_N, v, z) having the same values of h_N and v , the state $(h_N, v, 0)$ gives ε its smallest value (the energy minimum principle).*

In summary, it is perhaps important to stress that the extremum principles as formulated in this section are theorems, proved to follow from the existence of coordinate systems congruent with the geometrical structure of the space of nonequilibrium states.

5. A very simple example of Eqs. (3.2) and (3.3)₃

Given a three-dimensional, classical, moderately rarefied, simple, monatomic gas consisting of particles of unit mass, the fundamental equation (3.2) proposed by JOU *et al.* [5] is of the form

$$(5.1) \quad h = h_E(\varepsilon, v) - \frac{9k_B v^2}{16\varepsilon^2} \mathbf{P} \circ \mathbf{P} - \frac{27k_B v^2}{40\varepsilon^3} \mathbf{R} \circ \mathbf{R},$$

$h_E(\varepsilon, v)$ being given by Eq. (3.4'). Using this proposition, we see at a glance that Eqs. (3.3)₃ reduce to

$$(5.2) \quad z_\beta = \left[\frac{9k_B v^2}{16\varepsilon^2} \right]^{\frac{1}{2}} P_\beta, \quad \beta = 1, \dots, 5,$$

$$z_\beta = \left[\frac{27k_B v^2}{40\varepsilon^3} \right]^{\frac{1}{2}} R_\beta, \quad \beta = 6, \dots, 8.$$

Here P_β are components of \mathbf{P} with respect to the orthonormal basis in the space of symmetric traceless tensors of degree 2, and R_β are Cartesian components of \mathbf{R} .

A very simple relation (5.1) has the advantage of offering a major point of contact with the kinetic theory, as remarked by JOU *et al.* [5].

6. Final remarks

In this paper, we have treated only a simple macroscopic system: a system described by a finite set of real parameters $(y_1, \dots, y_r, z_1, \dots, z_s)$. As this case is the easiest to handle mathematically as well as the simplest in concept, we have reason to hope that

many results concerning it will have analogues for “nonequilibrium thermodynamics” with an infinite number of degrees of freedom ($r < \infty$, $s = \infty$).

For a kinetic theory of rarefied gases, by a simple application of the results obtained in Ref. [19], we can exhibit a pseudo-thermodynamic representation of Boltzmann’s entropy h . In other words, it is possible to express Boltzmann’s entropy h in terms of the specific energy ε , the specific volume v , and the countably infinite set of Hermite moments \mathbf{b}_α , $\alpha = 2, 3, \dots, \infty$. These moments are the expansion coefficients of the distribution function [19, 20]. *The resulting expression for h is such that the derivatives of h with respect to ε and v are functions independent of \mathbf{b}_α , $\alpha = 2, 3, \dots, \infty$.* The validity of this assertion will be demonstrated elsewhere.

Appendix A. A sketch of the Proof of the Theorem formulated in Sec. 3

In order to sketch the proof of our theorem, we shall introduce first for each $e \in E$ the specific coordinate system $\mu^e = (\mu_1^e, \dots, \mu_s^e)$ on a certain neighbourhood $\mathcal{N}(e)$ of $D(e, g_0)$ in $D(e, \mathbb{G}) \subset \mathbb{N}$; the existence of μ^e follows from the results established by the Morse critical point theory [3, 4, 21]. (In this context, we should note that $D(e, \mathbb{G})$ is diffeomorphic to \mathbb{G} and that $\dim \mathbb{G} = s$.) Then we show that the collection of coordinate maps $\{\mu^e : \mathcal{N}(e) \Rightarrow \mathbb{R}^s \mid e \in E\}$ can be “glued together in a smooth way”. This enables us to construct a diffeomorphism \mathfrak{z} from $\mathcal{N} := \bigcup_{e \in E} \mathcal{N}(e)$ onto a certain subset of $E \times \mathbb{R}^s$. Finally, using \mathfrak{z} and parametrizing a globally Cartesian manifold E , we arrive at the coordinate system on \mathcal{N} , the importance of which is manifest by the particularly simple form of the r.h.s. of Eq. (3.1).

1. STEP 1. *A construction of $\mu^e = (\mu_1^e, \dots, \mu_s^e)$.* Since $D(e, g_0)$ is a strict maximum point of the restriction of h to $D(e, \mathbb{G})$, we can draw upon results from the critical point theory [3, 4, 21]. According to this theory (cf., e.g., the lemma of MORSE on p. 493 in Ref. [4] and Proposition 3.10.4 on p. 144 in Ref. [3]), for each $e \in E$ there is a neighbourhood $\mathcal{N}(e)$ of $D(e, g_0)$ in $D(e, \mathbb{G})$ and a coordinate map on $\mathcal{N}(e)$, $\mu^e : \mathcal{N}(e) \Rightarrow \mathbb{R}^s$, $\mu^e = (\mu_1^e, \dots, \mu_s^e)$, such that if $h|_{\mathcal{N}(e)}$ denotes the restriction of h to $\mathcal{N}(e)$, then

$$(A.1) \quad h|_{\mathcal{N}(e)} = h(D(e, g_0)) - \sum_{\beta=1}^s (\mu_\beta^e)^2.$$

Clearly, the number s is equal to the dimension of the manifold $D(e, \mathbb{G})$ [$\dim \mathbb{G} = \dim D(e, \mathbb{G}) = s$]. From (A.1) it is not difficult to see that $\mu_\beta^e(D(e, g_0)) = \mu_\beta^e(e) = 0$ for any β .

2. STEP 2. *A construction of $\mathfrak{z} : \mathcal{N} \Rightarrow E \times \mathbb{R}^s$.* Now, using the collection of coordinate maps $\{\mu^e : \mathcal{N}(e) \Rightarrow \mathbb{R}^s \mid e \in E\}$, we can obtain a particular coordinate system on $\mathcal{N} := \bigcup_{e \in E} \mathcal{N}(e)$. However, before defining this system we shall recall some aspects of the construction of a chart $\mu^e : \mathcal{N}(e) \Rightarrow \mathbb{R}^s$ on the neighbourhood $\mathcal{N}(e)$ of e in $D(e, \mathbb{G})$ (cf., e.g., the reasoning of BISHOP and GOLDBERG directly after Proposition 3.10.3 in Ref. [3]). This construction starts by choosing a very specific basis for each $e \in D(e, \mathbb{G})$, namely a basis $\mathcal{R}(e)$ consisting of vectors orthonormal with respect to the Hessian H_e of $h_e := h|_{D(e, \mathbb{G})}$ at e .

The next stage in the analysis is to introduce a coordinate system at $e \in D(e, \mathbb{G})$ generated by $\mathcal{R}(e)$. (Concerning the method of obtaining this system, see the proof of Proposition 3.10.4 in Ref. [3].) Then the coordinate components of H_e are represented

in terms of the second derivatives of h_e . But $h : \mathbf{N} \Rightarrow \mathbf{R}$ is a sufficiently smooth function on \mathbf{N} . Thus, due to the definition of $\mathcal{R}(e)$, there exists a “smooth field of bases” $\{\mathcal{R}(e) \mid e \in \mathbf{E}\}$ such that the resulting collection of coordinate maps $\{\mu^e : \mathcal{N}(e) \Rightarrow \mathbf{R}^s \mid e \in \mathbf{E}\}$ can be “glued together in a smooth way”. This implies in turn that the mapping $\mathfrak{z} : \mathcal{N} \Rightarrow \mathbf{E} \times \mathbf{R}^s$ as given by

$$(A.2) \quad \mathfrak{z}(n) := (e, \mu_1^e(n), \dots, \mu_s^e(n)),$$

where $e = \pi(n)$, is a *diffeomorphism* from $\mathcal{N} := \bigcup_{e \in \mathbf{E}} \mathcal{N}(e)$ onto a certain subset of $\mathbf{E} \times \mathbf{R}^s$.

3. STEP 3. *A construction of the coordinate system on \mathcal{N} .* For the sake of simplicity, we assume that the manifold \mathbf{E} is “globally Cartesian”. In view of this assumption, \mathbf{E} has a global parametrization. Let $\nu = (\nu_1, \dots, \nu_r)$ be a global coordinate system on \mathbf{E} ; thus

$$(A.3) \quad \mathbf{E} \ni e \Rightarrow (\nu_1(e), \dots, \nu_r(e)) \in \mathbf{R}^r.$$

Combining (A.2) and (A.3), we obtain the coordinate map $\widehat{\mathfrak{z}} : \mathcal{N} \Rightarrow \mathbf{R}^{r+s}$ defined by

$$(A.4) \quad \widehat{\mathfrak{z}}(n) := (\nu_1(e), \dots, \nu_r(e), \mu_1^e(n), \dots, \mu_s^e(n)),$$

e being the image of $n \in \mathcal{N}$ under π . The collection of real numbers $(y_1, \dots, y_r, z_1, \dots, z_s)$ is said to determine (label) $n \in \mathcal{N}$ if

$$(A.5) \quad \begin{aligned} y_\beta &= \widehat{\mathfrak{z}}_\beta(n) := \nu_\beta(e), & \beta &= 1, \dots, r, \\ z_\beta &= \widehat{\mathfrak{z}}_{\beta+r}(n) := \mu_\beta^e(n), & \beta &= 1, \dots, s, \end{aligned}$$

where

$$e = \pi(n).$$

In other terminology, we may call the collection $(y_1, \dots, y_r, z_1, \dots, z_s)$ coordinates of $n \in \mathcal{N}$ in the chart $\widehat{\mathfrak{z}} : \mathcal{N} \Rightarrow \mathbf{R}^{r+s}$. Now, for each $e \in \mathbf{E}$, we set

$$(A.6) \quad h_E(\nu_1(e), \dots, \nu_r(e)) := h(e).$$

This relation defines a real-valued function h_E on the image of \mathbf{E} by $\nu = (\nu_1, \dots, \nu_r)$.

Given (A.1), the net upshot of the above considerations may be stated as the theorem of Sec. 3. ■

Appendix B. Background and connections with the theory of differentiable fibre bundles

The objective of this appendix is to summarize the basic assumptions which lead to Axioms (a)–(d) [cf. Sec. 2]. In our discussion, we omit the technical details.

1. Nonequilibrium thermodynamics seems always to rest upon the existence of

- (i) the set \mathbf{N} of nonequilibrium states;
- (ii) the proper subset \mathbf{E} of \mathbf{N} , consisting of all equilibrium states;
- (iii) the surjective mapping $\pi : \mathbf{N} \Rightarrow \mathbf{E}$.

From the physical point of view, the state $e \in \mathbf{E}$ is identified with a finite set of real numbers (y_1, \dots, y_r) such that $y_\beta, \beta = 1, \dots, r$, are conserved (extensive) quantities. In fact, without loss of generality, we can postulate that \mathbf{E} is a finite-dimensional manifold. The introduction of the surjective mapping $\pi : \mathbf{N} \Rightarrow \mathbf{E}$ enables us to define the equilibrium state $\pi(n) \in \mathbf{E}$ which has the same values of conserved quantities as $n \in \mathbf{N}$. The universal validity of this interpretation of $\pi(n)$ is a consequence of the following observation: even for systems not infinitesimally near to equilibrium, the y_β are well-defined observable quantities.

2. In thermodynamics, one usually limits attention to nonequilibrium states described by a finite number of degrees of freedom. Consequently, it is natural to assume that \mathbf{N} is a finite-dimensional manifold and that a triple $(\mathbf{N}, \mathbf{E}, \pi)$ forms a *bundle* [4].

3. Let $\pi^{-1}(\{e\})$ denote the set made up of all states $n \in \mathbf{N}$ consistent with a given equilibrium state e ; thus $\pi^{-1}\{e\} := \{n \in \mathbf{N} \mid \pi(n) = e\}$. This set is called a *fibre* at $e \in \mathbf{E}$ [4]. What seems to be true is that, in many cases, two different fibres are the same in all properties which concern only their structure as manifolds. It is this observation which we have used as our guideline in assuming that a triple $(\mathbf{N}, \mathbf{E}, \pi)$ has the structure of the *differentiable fibre bundle* [4].

4. Finally, we may assume that the differentiable fibre bundle $(\mathbf{N}, \mathbf{E}, \pi)$ is *trivial* [4]. Since the nontrivial fibre bundles do not appear very frequently in practice, this extra simplification can easily be accepted for many systems of physical interest. However, even if the bundle $(\mathbf{N}, \mathbf{E}, \pi)$ is not a trivial bundle, it is always possible to concentrate on discussing a distinguished *local trivialization* and then restrict attention to the domain of this local trivialization. It suffices to establish the theory on each such domain; hence without loss of generality we have postulated [cf. Axiom (c) in Sec. 2] that the set \mathbf{N} of all states is diffeomorphic to the Cartesian product of \mathbf{E} and the typical fibre \mathbf{G} [4].

5. Let D be a diffeomorphism from $\mathbf{E} \times \mathbf{G}$ onto \mathbf{N} . Our assumption that there exists exactly one element g_0 of \mathbf{G} satisfying $D(e, g_0) = e$ for each $e \in \mathbf{E}$ [cf. Axiom (d) in Sec. 2] is sufficiently general to represent most of the physically important situations. Then the definition of π by $\pi(D(e, g)) := e, g \in \mathbf{G}$, enables us to conclude that the equilibrium state $\pi(e)$ corresponding to $e \in \mathbf{E}$ is equal to e , as it should.

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